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Preparation of Carbon Nanotubes by Using Mesoporous Silica

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ABSTRACT

Carbon nanotubes were synthesized using several mesoporous silica templates with different pore sizes in order to investigate the possibility of controlling the diameter of carbon nanotubes by changing the pore size of the mesoporous silica. TEM observation confirmed that carbon nanotubes with uniform diameter can be obtained by the present method. However, it was found that it is difficult to prepare carbon nanotubes having diameter smaller than ~ 20 nm by the present method even if the template with small pore size is used.

INTRODUCTION

Owing to their new functional properties as electrode materials and hydrogen storage materials, carbon nanotubes attract rapidly growing attention [1]. Concerning the preparation of the carbon nanotubes, one of the most important problems is how to prepare nanotubes with desired form. Another significant problem is how to obtain such nanotubes in a large scale. Chemical vapor deposition (CVD) based synthesis of carbon nanotubes using an anodic aluminum oxide (porous alumina) membrane template is an interesting way to overcome the above mentioned problems [2, 3]. However, the tunable diameter of the nanotube prepared by the template carbonization method using porous alumina is limited to >20 nm. Furthermore, it is not easy to control the pore size and the thickness of the alumina membrane simultaneously. In the last decade, several techniques for making highly ordered periodic mesoporous silica with pore sizes of 2 - 50 nm have been developed [4, 5]. There are several types of pore alignment known as cubic, 3d-hexagonal and 2d-hexagonal. The 2d-hexagonal silica has cylindrical pores arranged in the honeycomb fashion. Using the ordered mesopores, nanostructured carbon materials have been tried to be synthesized and Jun et al.[6] succeeded in making a carbon replica of mesoporous silica. In the present study, we have tried to prepare carbon nanotubes using mesoporous silica by template carbonization method. We have investigated the possibility of controlling the diameter of carbon nanotubes by changing the pore size of the mesoporous silica.

EXPERIMENTAL DETAILS

Mesoporous silica with mesopores of 2 - 4 nm and 6 - 20 nm in diameter were synthesized in the presence of cetyltrimethylammonium bromide (CTAB, Aldrich) surfactant and triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) $P(EO)_{20}$ - $P(PO)_{70}$ - $P(EO)_{20}$ copolymer (Pluronic P123, BASF), respectively. Trimethylbenzene (TMB) was used as an organic swelling agent to enlarge the mesopore. The solution mixture was aged for 24 h at 353 - 383 K. Calcination was carried out by slowly raising the temperature from room temperature to 873 K.

CVD experiments were performed as follows. A mesoporous silica sample was evacuated in a SiO₂ tube at 383 K for 30 min. Then the reactor was filled with nitrogen gas and the temperature of the reactor was raised to 1073 K. Propylene and nitrogen gases were flowed for 1 h at flow rates of 1.25 cm³/min and 125 cm³/min, respectively. After the reaction, the reactor was cooled to room temperature. The mesoporous silica with carbon deposit was washed with an excess amount of HF solution at room temperature so as to dissolve silica.

The synthesized mesoporous silica and the CVD treated templates were characterized by XRD, N₂ adsorption-desorption isotherm measurements and TEM observation carried out on Rigaku RINT2200, Shimadzu GEMINI2375 and JEOL JEM2010, respectively.

RESULTS & DISCUSSION

The template designation used in the present paper is given in Table I.

The observed N₂ adsorption-desorption isotherms of the synthesized mesoporous silicas at 77 K are shown in Figure 1 (A). The pore size distributions determined from the isotherms by Barrett-Joyner-Halenda (BJH) method are shown in Figure 1 (B). The peaks in the distribution diagrams are very sharp except for the case of template P-3. Figure 2 shows the observed XRD patterns of the mesoporous silicas. All the observed peaks can be indexed with hexagonal unit cells and it indicates that the synthesized mesoporous silicas have cylindrical pores arranged in the honeycomb fashion. In the case of template P-3, no diffraction peak was observed. Assuming that template P-3 has a hexagonal unit cell of $a = 35$ nm (pore size 33 nm + wall thickness 2 nm), the d -values of 100, 110 and 200 diffraction peaks are greater than our XRD instrumentation limit (~ 13 nm).

Table I. Physicochemical properties, synthesis conditions of the synthesized mesoporous silica templates and the yield of carbon nanotubes

template No. ^a	TMB/surfactant weight ratio	aging temp. (K)	pore size ^b (nm)	$d_{(100)}$ (nm)	wall thickness ^c (nm)	yield of nanotubes
C-1	0.0	353	2.1	3.5	1.9	—
C-2	3.0	353	2.9	4.4	2.2	—
P-1	0.0	353	6.0	8.7	4.1	very low
P-2	0.0	383	9.6	10.4	2.4	low
P-3	0.5	353	33.0 ^d			high

^a Samples C-*m* and P-*n* were synthesized with CTAB and P123, respectively.

^b Calculated from adsorption branch of the N₂ isotherm by BJH method.

^c Calculated by a_0 -pore size ($a_0 = 2d_{(100)}/\sqrt{3}$).

^d Mean pore size observed by TEM is 20 - 30 nm.

Figure 3 shows TEM images of silica templates P-1 and P-3. The TEM images of template P-1 show that the mesopores are hexagonally arranged (Figure 3 (A)) and that the cylindrical pores are well aligned (Figure 3 (B)). On the other hand, although cylindrical pores are also observed in the TEM image of template P-3, the pores are not well aligned and the distribution of the pore size is relatively large. The pore sizes of template P-3 observed by TEM observation are 20 - 25 nm which is smaller than the value determined from the isotherm measurement. Physicochemical properties of the synthesized mesoporous silicas are summarized in Table I.

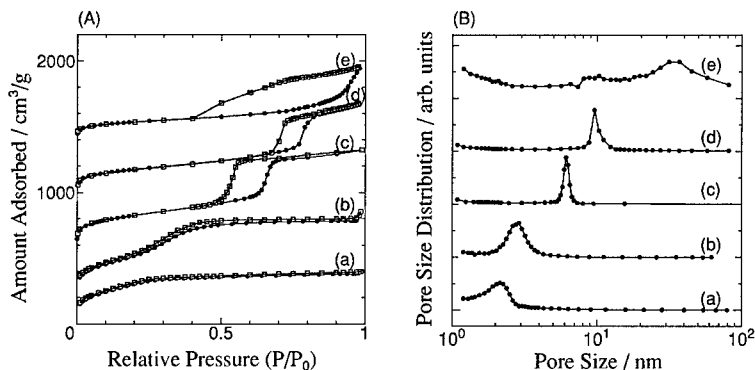


Figure 1. (A) N_2 adsorption-desorption isotherms for the prepared mesoporous silicas at 77 K. The data for (a) C-1, (b) C-2, (c) P-1, (d) P-2 and (e) P-3 are offset vertically by 0, 200, 600, 1000, and 1400 cm^3g^{-1} , respectively. (B) Pore size distributions for templates (a) C-1, (b) C-2, (c) P-1, (d) P-2 and (e) P-3.

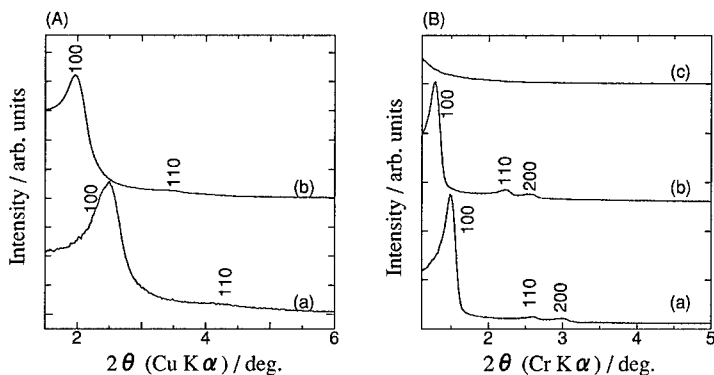


Figure 2. XRD patterns of templates (A)-(a) C-1, (A)-(b) C-2, (B)-(a) P-1, (B)-(b) P-2 and (B)-(c) P-3.

By CVD treatment, the color of the mesoporous silica changed from white to black and it indicates that the carbon deposition occurred on the surface of the silica. Figure 4 shows the XRD patterns of template P-2 before and after the CVD treatment. The ordered (hexagonal) structure of the mesoporous silica was maintained after the CVD treatment, although the diffraction peaks shifted slightly toward the higher angle side.

No carbon nanotube was found by TEM observation in the CVD treated templates C-1 and C-2 after silica templates were removed with HF solution. On the other hand, carbon nanotubes

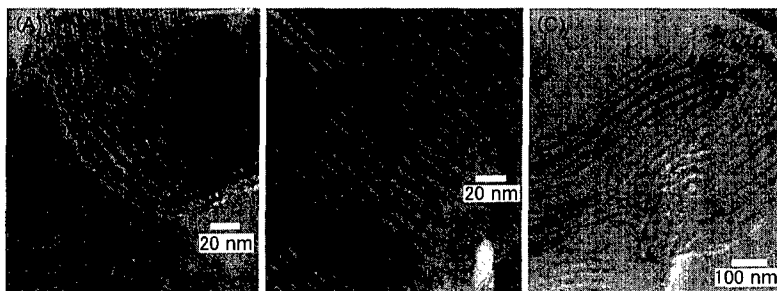


Figure 3. TEM images of silica templates (A) P-1, (B) P-1 and (C) P-3. (A) is recorded in the direction of the pore axis and (B), (C) are recorded in the direction perpendicular to the pore axis.

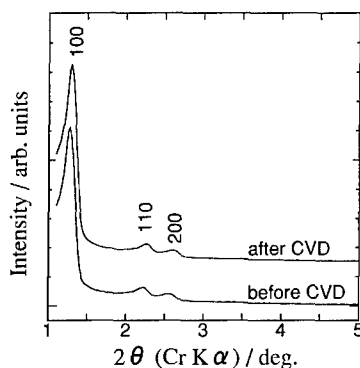


Figure 4. The observed XRD patterns of template P-2 before and after CVD treatment.

were found in the cases of templates P-1, P-2 and P-3. Although it is difficult to quantitatively determine the ratio of carbon nanotubes to the whole sample including amorphous carbon, the yields of carbon nanotubes are judged as very low, low and high for the cases of templates P-1, P-2 and P-3, respectively from TEM observation (Table I). The mean diameter of the carbon nanotubes prepared with template P-3 is ~ 30 nm, and agrees well with the mean pore size of the template. On the other hand, the diameters of the carbon nanotubes prepared with templates P-1 and P-2 are 10 - 20 nm and 15 - 25 nm, respectively, which are larger than the mean pore sizes of the silica templates determined from the isotherms. It is inferred that the deposition of carbon in small channels with diameter less than ~ 10 nm to form nanotubes is somehow mechanistically not possible, and that only those pores with larger diameters in templates P-1 and P-2 contributed to the formation of nanotubes. This also explains the low yield of nanotubes with templates P-1 and P-2. It was also found by high resolution TEM observation that the wall thickness of the nanotubes is 3 - 5 nm and that the walls of the carbon nanotubes are not well graphitized.

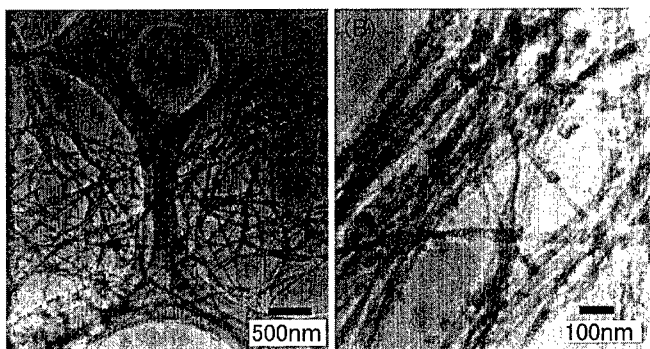


Figure 5. TEM images of the carbon nanotubes prepared using template P-3 as a template.

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